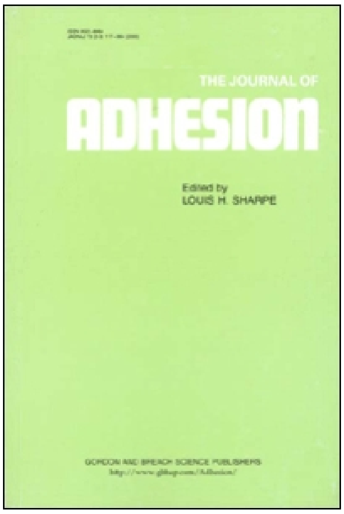

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Plasma Spray Treatments for Steel Adherends*

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Plasma-sprayed Ni–Cr and Ni–Cr–Zn coatings have been shown to protect steel adherends from corrosion in ambient and accelerated environments (up to eight days in alternate immersion and emersion in salt water for Ni–Cr–Zn coatings). The coatings exhibited excellent bondability to rubber and epoxy adhesives; peel and tensile button pull tests failed within the polymer for bonds formed on both "as-sprayed" surfaces and surfaces subjected to aggressive environments. The coatings have provided long hold times prior to bonding and are tolerant to processing and handling damage or defects.

KEY WORDS Surface treatments; Steel adherends; plasma-sprayed coatings; rubber-steel bonds; corrosion protection; adhesive bonding.

INTRODUCTION

Grit blasting is the most common procedure for preparing steel surfaces for adhesive bonding. It is simple, inexpensive and provides adequate bond performance for different alloys in many applications.[1-3] Various chemical etches or conversion coatings have been developed that give improved bond performance for a given application, but they often require stringent process controls and give very different results for different steel alloys.[1,2] One treatment that provides superior performance for one alloy may provide very poor performance for an alloy with different composition or heat treatment because of the formation of a loosely-adhering iron oxide "smut" or a smooth morphology that does not allow significant physical bonding (mechanical interlocking). As a result, grit blasting remains the most accepted treatment for steel adherends.

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* One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

Grit blasting has disadvantages because it provides no corrosion protection for steel. Unless it is done immediately before the primer/adhesive is applied, the surface must be protected from ambient conditions until bonding or primer application. Small parts can be stored in a low-humidity environment, but large parts often end up stored under ambient conditions and need protection from corrosion. Grease is a successful corrosion preventative. However, it is a bondline degrader that must be removed before bonding and the cleaned surface must be inspected to verify adequate cleanliness.[4] Currently, solvents used for degreasing are ozone-depleting compounds and are being phased out under the Montreal Protocol.

Elimination of these ozone-depleting compounds in adherend preparation can be achieved in three ways: replacement with aqueous cleaners or other environmentally-benign solvents, improvement of storage conditions (lower humidity and/or shorter time) so that corrosion does not have time to occur, or development of corrosion-resistant bondable surface treatments that do not require grease protection. The third approach has been investigated in developing plasma-sprayed coatings for steel adherends. Because this treatment eliminates the greasing, degreasing and inspection steps, it simplifies the manufacturing process and can reduce costs. In addition, it offers the environmental advantages of reduced atmospheric emissions and little or no waste water for treatment or disposal. (The water used for cooling during the plasma spray operation can be recycled and not released to water treatment plants.)

Plasma-sprayed coatings are used in a variety of applications where a coating tailored for specific properties is needed that may or may not be chemically or structurally similar to the base substrate. Metals, ceramics and polymers can all be deposited onto a similar range of substrates. Examples of use include wear resistance, thermal barriers, EMI/RF shielding, slip/slide resistance or enhancement and biocompatibility. As an adherend treatment, they have been demonstrated for titanium subject to high temperatures[1,5] and are being evaluated for aluminum.[6,7]

Six metal compositions have been evaluated as plasma-sprayed coatings onto steel. The two classes evaluated to the greatest extent (Ni–Cr and Ni–Cr–Zn) provide very good resistance to corrosion in ambient and high-humidity conditions and excellent bondability to rubber both before and after humidity exposure. In more severe environments, such as alternate immersion and emersion in salt water, the addition of zinc provided superior corrosion protection with no degradation of subsequent bond strength.

EXPERIMENTAL

Plasma-sprayed coatings were deposited onto either D6AC or 4130 steel that was grit blasted immediately prior to spraying using a virgin blend of alumina, fused silica, silicon carbide and crystalline silica. Several different coating compositions were tested:

Ni–Cr–6Al
77Fe–15Cr–6Al–2Mo
80Ni–20Cr

$76Ni-19Cr-5Zn$
$72Ni-18Cr-10Zn$
$64Ni-16Cr-20Zn$,

with the numbers indicating weight concentration of a given element. The first three powders were obtained from Metco. The last three were blended prior to spraying. The powder size was −120 +325 mesh. Spraying was achieved using a Metco 7M plasma gun with a 7MC control console, a 40-kW rectifier and a dual 4MP powder feeder. The carrier gas was Ar and the plasma was Ar/H. The gun is mounted on a GMF S-100 robot six-axis articulated-arm for controlled, reproducible coatings. No cover gas was used during spraying so that the local ambient for the spray would have been a mixture of air and argon. The coatings were formed with several passes of the spray in one of several patterns: horizontal, horizontal-vertical, and horizontal-vertical-diagonal. Coating thicknesses varied from 0.076 mm to 0.50 mm.

Three types of environmental exposure were used to evaluate the corrosion resistance of the coatings: long term (18 months) ambient laboratory exposure in Baltimore, Maryland, USA; high humidity (95% RH at 38°C for 30 days); and alternate immersion in 3.5% salt (NaCl) water (10 minutes immersed and 50 minutes emersed at 27°C for 8 days, according to ASTM G44). Panels were examined visually to note any rust formation and to compare with grit-blasted controls.

Bondability was determined with tensile button pulls using a room-temperature-curing, two-part epoxy (3M 1838 or 3M Scotch-Weld® 2216) and with peel and tensile button tests using bonded rubber. In the case of D6AC substrates, acrylonitrile butadiene rubber (NBR) was bonded to the steel using Chemlok 205® primer and Chemlok 233® adhesive (Lord Corp., Erie, PA, USA). For experiments in which the steel was environmentally exposed, bonds were formed following the exposure. Peel tests were performed at 180° at 2 mm/s; tensile button tests were performed at 0.08 mm/s. For 4130 steel substrates, EPDM rubber was bonded using Chemlok 205® primer and Chemlok 252® adhesive. The EPDM included a steel scrim layer coated with the primer and adhesive to strengthen the rubber and reduce stretching during the peel test. This scrim also allowed greater stress to be applied to the bondline while peeling. These tests were performed at 90°. The strength measurements represent the average of six specimens for the rubber bonds and three for the epoxy bonds.

RESULTS

Corrosion Resistance

The initial corrosion test was long-term ambient exposure. A 0.076-mm-thick Ni–Cr–Al coating on 4130 steel was stored in the laboratory for 18 months. At the end of this period, there were no signs of rust on the coating although the back, edges and uncoated corners exhibited significant dark, rusted areas due to the ambient humidity in Baltimore, MD.

The next level of corrosion testing involved 30 days of exposure to the previously-described high-humidity environment. The 0.076-mm-thick Ni–Cr–Al coating was tested along with 0.13-mm-thick Fe–Cr–Al–Mo and 0.18-mm-thick Ni–Cr coatings. The two thicker coatings passed this humidity test with no visible rust spots. In contrast, the grit-blasted control specimen was totally covered with bright orange rust. Even with only 0.076-mm thickness, the Ni–Cr–Al coating showed significant improvement in corrosion resistance but, nonetheless, exhibited several rust spots. The thickness of the coating appeared to have a greater effect on corrosion resistance than composition. This might be expected from the possibility of interconnected porosity in the thinner coatings, which would allow the environment to penetrate the coating and attack the substrate. Typical porosity is shown in the cross-section micrograph of a Ni–Cr–Zn coating in Figure 1.

The Ni–Cr coating was chosen for further high-humidity tests to evaluate the effect of thicknesses and spray pattern on the corrosion resistance. Coatings with several different thickness and spray patterns were exposed for 30 days. The multidirectional horizontal-vertical-diagonal pattern gave the best results for a given thickness, most likely because of a reduction in interconnected porosity. For these specimens, thicknesses of 0.15 mm appeared adequate for protection from humidity. In comparison, the grit blasted controls were covered with rust in a few days.

In contrast to their behavior in humidity, Ni–Cr coatings even at thicknesses up to 0.5 mm did not protect the steel in the much more severe alternate immersion and emersion salt water tests for more than 2 to 3 days. Dramatic improvements in corrosion protection were obtained by adding small amounts (5, 10, or 20%) of zinc to the Ni–Cr powder to protect the steel cathodically. Each of these specimens survived 8 days in the alternate immersion/emersion salt water with no rust spots

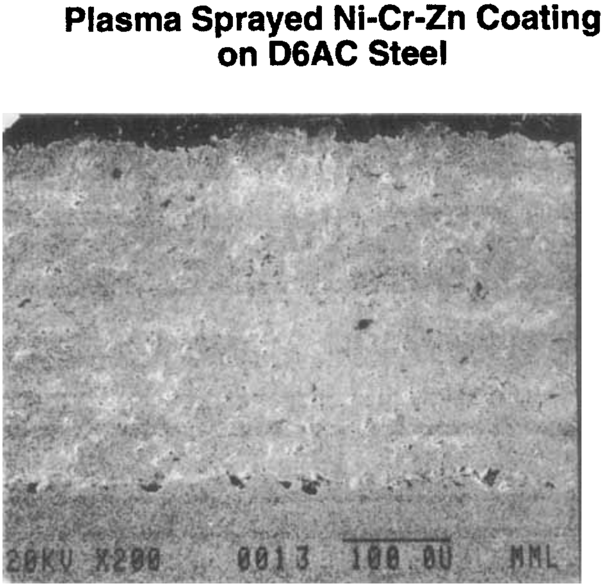


FIGURE 1 Cross section micrograph of a Ni–Cr–Zn coating showing the presence of porosity that limits the corrosion protection. The apparent voids at the interface are imbedded alumina particles from the grit blasting.

forming although a white deposit (presumably $Zn(OH)_2$) appeared on the coating, especially for the higher-Zn-concentration specimens. For the first several days, the cathodic protection provided by the zinc was sufficient to protect the control grit-blasted area of the specimen for approximately 5 millimeters away from the coating. However, at the end of the test, the entire grit-blasted area was rusted.

Bondability

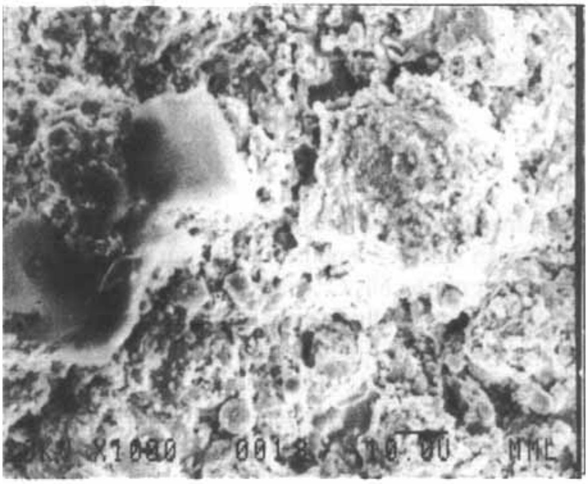
The as-received, plasma-sprayed surfaces are very rough on a visible to near-microscopic scale with a mean surface roughness of 12 µm as measured by a hand-held Surtronic 10 profilometer on the Ni–Cr coating. For comparison, the roughness of a grit-blasted steel surface is typically 2–6 µm.[6] Micrographs of plasma-sprayed and grit-blasted surfaces are given in Figure 2. Both surfaces demonstrate a large scale convoluted and irregular roughness. The features on the grit-blasted surface are generally angular while those on the plasma-sprayed surface are more rounded. In each case, the convoluted morphology provides adequate opportunity for physical bonding or mechanical interlocking with the rubber. The morphology of a grit-blasted surface is dependent on the type of grit used, its velocity and angle and other factors.[6] The surface shown in Figure 2 was identical to the surface grit-blasted immediately prior to plasma spraying. Other experiments using epoxy aerospace adhesives with either aluminum or titanium adherends and the same grit-blasting procedure indicate that these grit-blasting parameters are close to optimum for adhesive bonding applications.[7] Surfaces prepared in this manner provide wedge test durability results superior to surfaces prepared using conventional grit-blasting operations.

Peel and tensile tests using NBR rubber bonded to fresh Ni–Cr surfaces gave identical results for plasma-sprayed and grit-blasted adherends—failure within the rubber. For both surface preparations, peel strengths averaged 25 kN/m and tensile strengths averaged 4.4 MPa. Peel tests using EPDM also gave identical results for plasma-sprayed and grit-blasted surfaces—4.7 kN/m with cohesive failure within the rubber. (Note that the two peel tests are with different materials and at different angles; thus, the peel strength values are not directly comparable.) Table I summarizes the bond tests for plasma-sprayed steel.

Another test of the bondability of the coating to an adhesive and the adhesion of the coating to the substrate was provided by the tensile buttons using 3M 1838 epoxy adhesive. Again, the failure was entirely cohesive within the adhesive with tensile strengths being greater than 27 MPa. As such, this value represents the lower limit for the cohesive strength of the coating, the adhesion between the coating and the adhesive and the bond between the coating and the substrate.

Several tests were also performed to evaluate the bondability of the coatings after various environmental exposures. Following the 18-month ambient exposure, tensile buttons were attached to the plasma-sprayed Ni–Cr–Al coating using epoxy adhesive without solvent cleaning or any other form of surface preparation. The tensile pull strengths were greater than 27 MPa with cohesive failure within the epoxy. These results were identical to those obtained shortly after spraying, indicating that exposure to the ambient, humid conditions in the Baltimore, Maryland, area for

Plasma Sprayed Ni-Cr-Zn Coating



Grit Blasted D6AC Steel

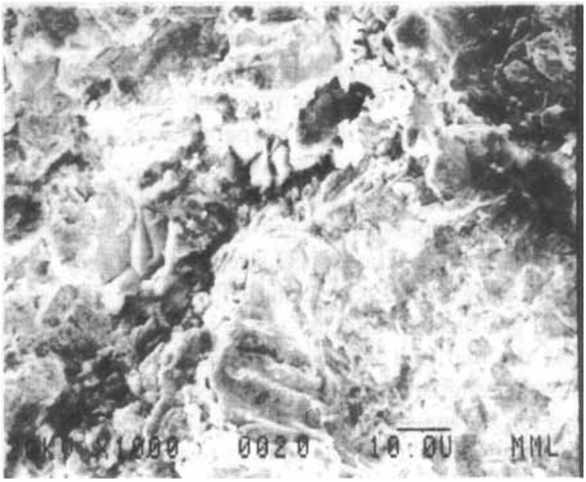


FIGURE 2 Micrographs showing the surface morphology of grit-blasted and plasma-sprayed (Ni–Cr–Zn) surfaces. Both show considerable roughness with sufficient convoluted features to provide good bonding with rubber.

18 months did not affect the bondability of the coating. The findings also suggest that the bond was insensitive to any surface contamination that might have occurred during this period.

Peel tests using EPDM rubber were performed on 4130 steel with Ni–Cr coatings that had been exposed to high humidity for 7 and 30 days and subsequent ambient exposure for several months. Peel strengths identical to that of an as-received panel

TABLE I
Bond Strength Measurements for Plasma Sprayed Steel

Coating	Steel	Polymer	Exposure	Test	Strength	Failure mode
Ni-Cr	D6AC	NBR	fresh	180°peel	25.9 kN/m	rubber
Ni-Cr	D6AC	NBR	fresh	tensile button	4.33 MPa	rubber
Ni-Cr	4130	EPDM	fresh	90° peel	4.6 ± 0.2 kN/m	rubber
Ni-Cr	4130	EPDM	7 d, humidity	90° peel	4.9 ± 0.5 kN/m	rubber
Ni-Cr	4130	EPDM	30 d, humidity	90° peel	4.9 ± 0.4 kN/m	rubber
Ni-Cr-Al	4130	1838 epoxy	fresh	tensile button	>27 MPa	epoxy
Ni-Cr-Al	4130	1838 epoxy	18 m, ambient	tensile button	>27 MPa	epoxy
Ni-Cr-20 Zn	D6AC	2216 epoxy	8 d, alternate immersion	tensile button	18 ± 0.5 MPa	epoxy

(4.7 kN/m) were obtained with failure again in the rubber indicating no decrease in the bondability of the surface with exposure (within the test limitations of rubber peel measurements). Interestingly, peel strengths of grit-blasted controls exposed for 30 days were only slightly reduced (4.4 kN/m) with failure remaining cohesive within the rubber even though considerable rust was present on the surface and was not removed prior to bonding.

A more severe test of post-exposure bondability was the use of tensile pull buttons on the 64Ni-16Cr-20Zn specimen after 8 days of alternate immersion/emersion in salt water. This specimen was chosen as a worst case example with the greatest amount of zinc oxide/hydroxide present on the surface. The tensile pull strength (using 3M ScotchWeld 2216® epoxy adhesive) was 18 MPa with cohesive failure in the epoxy. Once again, the environmentally-exposed plasma-sprayed surfaces showed no signs of degraded bondability. In contrast, identical button pulls bonded to the grit-blasted control area failed within the rust layer at low strengths (< 2 MPa) as would be expected from a severely rusted surface with poorly adherent corrosion products.

DISCUSSION

The ability to deposit coatings with tailored properties is one of the major advantages of plasma spraying. Surface treatments are not limited to chemical or physical modifications of the substrate material as is the case with grit-blasting, etching, anodization, or conversion coating. The coating properties can be optimized for a given application. In this case, for example, the coating was tailored to achieve maximum bondability and corrosion resistance for steel substrates.

The bondability of freshly plasma-sprayed surfaces is the result of the convoluted roughness that allows considerable physical bonding and provides a strong interface regardless of presence or strength of chemical bonds. Similar bondability of plasma-sprayed coatings has been demonstrated for titanium[5,6] and aluminum[6,7] adherends. For the current application of rubber-steel bonds, the degree of porosity and the scale of the morphological features and, hence, the density of physical bonds are not as critical as high-strength epoxy-aluminum or titanium joints. The cohesive strength of the rubber is the limiting factor in this case and it does not subject the interface to stresses as high as those found in epoxy structural joints.

The ability of plasma-sprayed coatings to protect against corrosion is less certain because of the inevitable porosity (Fig. 2) that, if interconnected, can allow moisture or other fluids to reach the substrate and initiate attack. The Ni–Cr coating was a sufficient barrier to moisture to protect the surface during the 30-day test period in high humidity and for a much longer time in the less severe ambient environment. In the alternating exposure to salt water, the Ni–Cr coating was not sufficient by itself, but was successful over an 8-day test period when supplemented by small additions of zinc as a sacrificial anode. By analogy, this coating should be protective indefinitely under ambient conditions and for extended periods in coastal environments.

The use of zinc to protect steel cathodically is very common, but its use as part of an adherend preparation is not. Because the zinc is sacrificed in the protection process, one would not normally use it at a bondline; its conversion to $Zn(OH)_2$ is akin to the hydration of Al_2O_3 to AlOOH, which is the chief mode of failure of aluminum bonds exposed to moisture.[1,8] The two differences in the present case that allow good bondability after alternate immersion/emersion is the relatively small amount of Zn present in the coating and the formation of the bond after environmental exposure instead of before exposure. The Ni–Cr component of the coating provides the skeletal framework that forms the physical bonding with the polymer and allows stresses to be transferred across the interface. In this way, the Ni–Cr–Zn coating is well suited as a stable adherend preparation—the Ni–Cr forms the structure of the bondline while the Zn provides additional corrosion protection. For our tests, as little as 5% Zn was sufficient; at that level, it is unlikely that the formation of that amount of $Zn(OH)_2$ would cause bond failure even if its formation occurred after the bond was made.

The Ni–Cr–Zn coating offers several advantages as an adherend preparation. The high bond strengths both before and after accelerated environmental exposure demonstrate its bondability. Its stability suggests long hold times between preparation and bond formation are feasible, with at most a cleaning operation to remove any gross surface contamination deposited on the surface during the storage period. In addition, the temporary protection of the grit-blasted surface near the coating during alternate immersion/emersion suggests that the coating would be tolerant of defects and handling damage. If a scratch, holiday, or other defect was present, the adjacent coating would still provide cathodic protection of the exposed area. Such defect tolerance is not possible with a surface treatment providing corrosion protection solely by use of a barrier layer.

Note added in proof. Tensile button pulls were performed on the original plasma sprayed panel after it had been stored under laboratory ambient conditions for five years. Failure was again cohesive in the epoxy adhesive with peel strengths averaging 26 MPa.

SUMMARY AND CONCLUSIONS

Plasma-sprayed Ni–Cr–Zn coatings on steel can provide excellent corrosion protection in both high humidity and salt water environments. The surface is very rough to allow considerable mechanical interlocking with a polymer. Bondability of the coating to rubber and epoxy adhesives is excellent both initially and after accelerated environmental exposure with bond strengths being greater than the cohesive strength of the polymer in all cases tested. The coating is robust in that it tolerates defects that may occur during processing and handling and still protects the surface. Very long hold times before further processing are predicted based on the ambient exposure for 18 months and more severe accelerated environmental exposures.

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